

Unusual Coarsening During Phase Separation in Polymer Systems

C. B. Muratov

*Courant Institute of Mathematical Sciences, New York University,
251 Mercer St., New York, NY 10012*

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We introduce a kinetic model of coarsening of transient polymer networks during the intermediate stages of phase separation in polymer systems. The model explicitly takes into account the effect of the connectivity of polymer chains. We show that during the intermediate stages the size of the droplet grows according to an unusual coarsening law $R \sim t^{1/(d+3)}$. When the network structure breaks up, the coarsening law may cross over to $R \sim \ln t^{-1}$, until only at very late stages the Lifshitz-Slyozov coarsening law $R \sim t^{1/3}$ is recovered.

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Kinetics of phase separation in polymer systems is an important problem both from the scientific and technological point of view. Phase separation in such systems is driven by the difference in the chemical potential of the species [1–3], so at long times the kinetics of this process should fall in the same dynamic universality class as simple fluids [4]. This is indeed observed in the experiments on phase separation in polymer solutions and blends (see, for example, [5–7]). Nevertheless, because of the large size of polymer molecules the universal kinetics of phase separation may not be seen until very late times. Recent experiments [8,9] and molecular dynamics simulations [10] showed that in the intermediate stages of phase separation interconnected network structures may be observed. In other words, in the intermediate stages the system may become a *transient gel* [11], so its connectivity should play crucial role in the kinetics of phase separation.

In this Letter, we introduce a kinetic model of coarsening of polymer networks during the intermediate stages of phase separation. For definiteness, we will consider phase separation in concentrated polymer solutions undergoing a deep quench into the unstable state. We will show that the connectivity of the droplets of polymer-rich phase entirely changes the transport mechanism which determines the coarsening of droplets, resulting in an unusual coarsening law: $R \sim t^{1/(d+3)}$. This coarsening will arrest when the distance between the droplets reaches the value of the order of the radius of gyration R_g of the polymer chain before the quench, when the network structure will break up. After that, a much slower coarsening mechanism may switch on resulting in the coarsening law $R \sim \ln t^{-1}$. Only when the distance between droplets becomes of the order of the length of the fully stretched polymer chain, the coarsening will cross over to the conventional Lifshitz-Slyozov mechanism with $R \sim t^{1/3}$ [12].

When a polymer solution is quenched deep into the unstable region, spinodal decomposition occurs. After a relatively short transient period the system segregates into polymer-rich droplets of size of order a , where a is

the statistical segment length. Due to repulsive interaction between the polymer and the solvent polymer-rich droplets will exert attractive force of order T/a on the chains that cross their interfaces, pulling them into the droplets. Here two qualitatively different situations are possible. If the chains are not very long, the initial transient time will be enough for a droplet to pull in all the chains that come into contact with it, so after the transient the morphology of the droplets will be disconnected. In contrast, if the length of the chains is large enough, during the initial transient time the chains will be pulled into droplets until they will become fully stretched between the points of entanglement (Fig. 1). The reason for the latter is that when the chains are sufficiently long (or, equivalently, when the distance between the droplets is smaller than the radius of gyration R_g of the chain before the quench), a single chain may initially become a part of several droplets at the same time. Therefore, after the transient period, the morphology of the droplets will be connected. In a stretched state the conformation of a chain connecting a pair of droplets will be Gaussian with the effective segment length $aN_e^{1/2}$, where N_e is the average number of segments between the entanglement points before the quench (Fig. 1).

After the network morphology is formed, the motion of the chains will significantly slow down since on average the force acting at the point of attachment of the chain at one droplet will be compensated by the opposite force from another droplet, thus stretching the chain. The total force, however, will not be exactly equal to zero since the droplets between which a piece of the chain is stretched will not generally have the same radii. The latter will result in the difference of the surface pressures leading to the net force of order T/R , where R is the characteristic radius of a droplet, acting on the stretched piece of the chain (Fig. 1). So, a piece of the chain connecting a pair of droplets will slowly creep along itself from the droplet with smaller radius to the droplet with greater radius (Fig. 1) with the speed of order

$T\mu a^2 N_e^{1/2} / (RL^2)$, where μ is the mobility of an individual segment and L is the distance between the connected droplets. In estimating the speed of the chain we assumed that the friction force is proportional to the number of segments $L^2 / (N_e^{1/2} a^2)$ in the chain piece. This creeping motion should result in the transport of segments from the smaller droplets to the larger ones and, therefore, lead to their coarsening. Note that the connectivity of the chains results in the *nonlocal* mass transport, since for the latter the creep of the chain is equivalent to taking monomers from one droplet and putting them instantaneously into the other.

The mass current into a droplet is proportional to the average speed of the chains into that droplet and the number of chains that come into it. A peculiar feature of the considered transport mechanism is the fact that as long as the average droplet size is smaller than the distance $aN_e^{1/2}$ between entanglements, the number of chains that come out of a given droplet is independent of time (see Fig. 1). So, the current into the droplet is simply proportional to the average speed of the chains. This is in contrast with the conventional Lifshitz-Slyozov mechanism in which the mass current into the droplet is proportional to the surface area of the droplet [12]. Writing the conservation of mass for a droplet of size R , using the expression for the velocity of a stretched portion of a chain and taking into account the conservation of volume fraction of the polymer-rich phase, we obtain that on average $R^{d-1} dR/dt \sim 1/R^3$. This suggests that the considered mechanism will result in the average droplet size growing as $R \sim t^{1/(d+3)}$ and self-similar growth of the droplet morphology.

Let us demonstrate that this self-similar growth should actually take place for low polymer volume fraction when the system contains many droplets of different sizes. For simplicity, let us consider three-dimensional system. Then the droplets can be assumed to be spherical and uniformly distributed over space. Let us introduce the distribution function $f(R, t)$ normalized in such a way that the integral $\int f dR$ gives the number of droplets per unit volume. Since after the initial formation of the network no droplets will be further created, the function f must satisfy Liouville equation

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial R}(mvR^{-2}f), \quad (1)$$

where m is the number of chains coming out of a droplet and v is the average speed of the chains into the droplet. As was already pointed out, on the time scale of the considered coarsening process the number m of chains coming out of a droplet is time-independent. At the beginning of coarsening all droplets have roughly the same size of order a , so on average the number m will be the same for all droplets. Therefore, in the following we will treat m as a constant of order 1. The average velocity v can be written as

$$v = \int dP(R', L) \frac{1}{L^2} \left(\frac{1}{R'} - \frac{1}{R} \right). \quad (2)$$

Here and in Eq. (1) an appropriate non-dimensionalization has been performed. In Eq. (2) the term $dP(R', L)$ is the probability that the droplet of radius R is connected with the droplet with radius R' at distance L , the term $1/L^2$ comes from the dependence of the mobility of the stretched portion of the chain on its length, and the term $(1/R' - 1/R)$ is the driving force.

In the following we will assume that the chains connect different droplets at random. Let us measure distances relative to the droplet of radius R . Since the chains are highly stretched, the probability dP is essentially the probability that a random walk of step $aN_e^{1/2}$ starting from the origin terminates at a droplet of size R' at distance L while not crossing any other droplets on its way. This probability is the product of two parts: $dP(R', L) = dP_1(R', L)P_2(L)$, where $dP_1(R', L)$ is the probability that a droplet of size R' at distance L is connected to the origin disregarding the effect of other droplets, and P_2 is the probability that the chain connecting these droplets did not cross any other droplets. Since by assumption the same number of chains comes out of all droplets regardless of their size, the probability dP_1 can be written as

$$dP_1(R', L) = CL^2 f(R') dR' dL, \quad (3)$$

where C is the normalization constant. It is not difficult to show that for a random walk in the presence of small spherical obstacles with the distribution function f

$$P_2(L) = e^{-\kappa L^2}, \quad \kappa = 4\pi \int R f dR. \quad (4)$$

The constant C is determined by the condition $\int dP = 1$. This gives us

$$C = \frac{4\kappa^{3/2}}{\sqrt{\pi} \int f dR}. \quad (5)$$

Note that κ and C are determined by the distribution f and therefore are functions of time.

Writing the probability dP in the above form essentially constitutes a self-similarity assumption about the connectivity of the network as a function of time. This should be a good assumption since as smaller droplets collapse during coarsening, the chains that came out of them simply reconnect between other droplets.

Having now calculated dP , we can substitute it to Eq. (2) and integrate over L . As a result, we can write the expression for v (absorbing m into it) in the form

$$v = \Lambda \frac{\int R f dR}{\int f dR} \int dR' f(R') \left(\frac{1}{R'} - \frac{1}{R} \right), \quad (6)$$

where $\Lambda = 6m\phi$, ϕ is the volume fraction of the polymer-rich phase and the normalization of f was changed to

$\int R^3 f dR = 1$. The constant Λ determines the rate of the coarsening process. In the following we will absorb it into the definition of t . Note that according to Eq. (6) we have $\int v f dR = 0$, meaning the conservation of the overall mass of droplets (assuming that the volume fraction of the chains outside the droplets is negligible).

Equations (1) and (6) are of the same type as those studied by Lifshitz and Slyozov in the theory of coarsening by evaporation-condensation mechanism [12] and can be treated in the same way. Let us introduce a similarity ansatz $f(R, t) = t^{-2/3} F(Rt^{-1/6})$ into Eqs. (1) and (6). Introducing $x = Rt^{-1/6}$, we obtain an equation

$$4F + xF' = 6a_1 \frac{d}{dx} [F(a_2 x^{-2} - x^{-3})], \quad (7)$$

where the constants a_1 and a_2 are given by

$$a_1 = \int_0^\infty x F dx, \quad a_2 = \frac{\int_0^\infty x^{-1} F dx}{\int_0^\infty F dx}, \quad (8)$$

and the prime denotes differentiation with respect to x . The function F is normalized according to

$$\int_0^\infty x^3 F dx = 1. \quad (9)$$

Note that from the condition of the conservation of mass $\int v f dR = 0$ follows that the second of Eq. (8) is identically satisfied for any solution of Eq. (7).

Equation (7) can be straightforwardly integrated

$$F = A e^{-\int_1^x \frac{4y^4 + 12a_1 a_2 y - 18a_1}{y^5 - 6a_1 a_2 y^2 + 6a_1 y} dy}, \quad (10)$$

where the constant A is determined via Eq. (9). As in the Lifshitz-Slyozov theory [12], the solution that is selected at long times from the extended initial distribution should vanish alongside with all its derivatives at some $x = x^*$. This is only possible if the integrand of Eq. (10) has a double pole at this value of x . The analysis shows that this situation is realized if for a given value of a_2 we have $x^* = 4/(3a_2)$ and $a_1 = 2^7/(3^4 a_2^4)$. Then, the constant a_1 is calculated so that the first of Eq. (8) is satisfied. We have done this calculation numerically and found that $a_2 = 1.1027$ and $A = 4.0446$. The solution for F in this case is shown in Fig. 2. From this solution one finds that the average radius of the droplet grows as $\langle R \rangle = 0.94t^{1/6}$, while the average droplet density decays as $\langle n \rangle = 1.14t^{-1/2}$. Note that the polydispersity of the droplets during coarsening is rather small, we have $\langle (R^2) - \langle R \rangle^2 \rangle / \langle R \rangle^2 = 0.023$ in $d = 3$.

Observe that in his pioneering paper on phase separation in polymer systems de Gennes proposed the coarsening law $R \sim t^{1/5}$ for $d = 3$ in the early stages of coarsening [13]. In [13] the transport is due to diffusion of chains between the droplets with Rouse mobility of the chains [14] which is taken to depend on R . However, it is clear that Rouse diffusion of the chains will be suppressed when the distance between the droplets becomes

comparable to the distance between entanglements soon after the onset of phase separation. After that the system becomes a transient gel, so the coarsening mechanism should change to the one studied by us. Note that the importance of highly stretched chains for phase separation kinetics was pointed out already in [13].

The coarsening law $R \sim t^{1/6}$ obtained by us for three dimensions is in very good agreement with the experimental results of Tanaka who finds that $R \sim t^{0.15}$ for a phase separating polymers solution in the network state. Also, the coarsening law $R \sim t^{0.23}$ observed in experiments on coarsening of thin diblock copolymer films [15,16] is in good agreement with our result for two dimensions.

Note that in the analysis of coarsening we assumed that the number of chains coming out of a droplet is independent of time. This is a good assumption as long as the size of the droplet is smaller than the distance $aN_e^{1/2}$ between the entanglement points. At the onset of the considered coarsening process the distance between the droplets is of order $aN_e^{1/2}$, so the radius of a droplet will be much smaller than that in the case of low polymer volume fraction. In fact, the smallness of the polymer volume fraction is the necessary condition for the considered coarsening mechanism to be realized. Note, however, that before the size of a droplet becomes comparable to $aN_e^{1/2}$, the distance between the droplets may reach the value of the order of the radius of gyration R_g of the chains before the quench, so the network will break up. The latter is observed in the late stages of coarsening in the experiments of Tanaka [9].

After the breakup of the network one would expect that the conventional Lifshitz-Slyozov transport mechanism turns on resulting in $R \sim t^{1/3}$ growth law. Note, however, that the rate constant for such a mechanism will be extremely small for deep quenches [13] (for recent developments, see also [17]). This is due to the fact that Lifshitz-Slyozov mechanism would require an evaporation of an entire chain from a droplet, which then diffuses through the matrix to another droplet. For deep quenches the free energy cost of such a fluctuation will be of order TN , where N is the polymerization index, so the rate at which such an event would occur will be proportional to e^{-N} which rapidly becomes very small as N increases. Note, however, that this is not the only possibility for a transport of chains if the droplets are close enough. Instead of the whole chain coming out of a droplet, a portion of a chain containing Z segments may come out. Furthermore, this portion of a chain can be highly stretched, so the free energy cost of such a fluctuation will be of order $TZ + TL^2/(a^2 Z)$, where a is the statistical segment length and L is the distance the chain is stretched. For a given L this expression has a minimum at $Z \sim L/a$, so the free energy cost of having a chain piece sticking out a distance L from the droplet is of order $TL/a \ll TN$ for $L \ll Na$. On the other hand, if the distance between the droplets is of order L , there is a

good chance that such a protruding chain piece will come in contact with another droplet and stick to it. If this happens, after a relatively short time the chain will become stretched, and the transport mechanism discussed above will switch on (Fig. 1) leading to a transfer of the entire chain from the droplet with smaller radius to the one with the greater radius. The rate of such a process will be proportional to $e^{-L/a}$, so one would expect this to lead to coarsening of the form $L \sim \ln t^{-1}$. Of course, when the distance between the droplets becomes comparable to Na , such a process will no longer be feasible, so the conventional Lifshitz-Slyozov mechanism with the rate proportional to e^{-N} will be realized.

In determining the dominant coarsening mechanism in a real system, one should also consider the coalescence mechanism [18]. It is clear that while the system is in the network state this mechanism cannot work since the stretched chains prevent the droplets from executing Brownian motion. On the other hand, when the network breaks up, the mechanism discussed above quickly becomes very slow, so in polymer solutions, where the mobility of the droplets will be high, coalescence should become the dominant transport mechanism. This conclusion is supported by recent experiments on phase separation of relatively low molecular weight polymer blends [19]. In contrast, in polymer melts the mobility of the droplets will be significantly smaller, so one would expect the mechanism discussed in the preceding paragraph to be the dominant one. Notice that because the latter is very slow, in experiment this can be seen as an arrest and intermittency of the droplet growth. This is indeed observed in the experiments on polymer melts [20,21].

In conclusion, we have demonstrated that polymer chain connectivity may have significant effect on the kinetics of phase separation in polymer systems resulting in the unusual coarsening laws in the intermediate stages.

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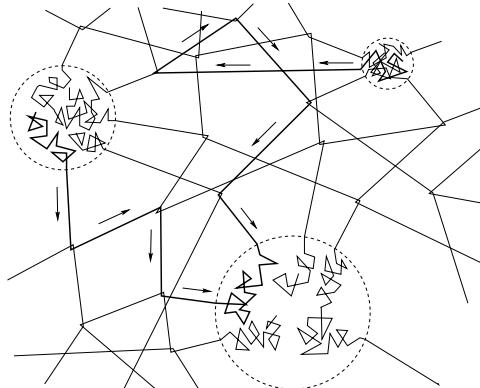


FIG. 1. Transient polymer network. Thick line shows a test chain. The arrows indicate the motion of the test chain.

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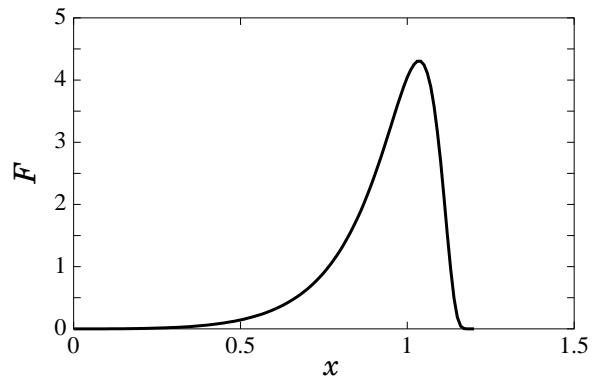


FIG. 2. The distribution $F(x)$ for $d = 3$.